Measurement of Henry's Law Constants for Acetone, 2-Butanone, 2,3-Butanedione, and Isobutyraldehyde Using a Horizontal Flow Reactor

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Henry's law constants for acetone, 2-butanone, 2,3-butanedione, and isobutyraldehyde were investigated using a horizontal flow reactor coupled to a molecular beam mass spectrometer. These organics belong to a class of oxygenated compounds that are increasingly used as industrial solvents and were chosen to better understand and evaluate their atmospheric fate. All experiments were performed at atmospheric pressure and temperature over the range of (275 to 298) K. The Henry's law constants H_x at $T = 298$ K are the following (in units of $\mathrm{M{\cdot}atm^{-1}}$): acetone, (26 ± 6); 2-butanone, (2.7 ± 0.3); 2,3-butanedione, (57 ± 8); and isobutyraldehyde, (0.60 ± 0.10). The $-\mathrm{d}\ln H_x/\mathrm{d}(1/T)$ values are the following (in units of K): acetone, (6400 ± 1600); 2-butanone, (12 000 ± 5000); 2,3-butanedione, (6700 ± 2400); and isobutyraldehyde, (4500 ± 2900). The uncertainties listed above are $\pm 2\sigma$ and have been calculated using a propagation of errors analysis.

Introduction

Four oxygenated hydrocarbons, namely, acetone, 2-butanone, 2,3-butanedione, and isobutyraldehyde, are either emitted from biogenic[1] and anthropogenic sources[1,2] or produced as reaction intermediates in the atmospheric photooxidation of volatile organic compounds (VOC).[3,4] Because the four oxygenates listed above are miscible in water, they can either be taken up by hydrometeors (i.e., aerosols, cloud droplets, rain, fog, etc.) or form secondary aerosols (SOA) with potential implications for atmospheric chemistry, wet deposition, health, and climate.[3] For example, the upper tropospheric photolysis of acetone, the most abundant ketone in the atmosphere, may more efficiently produce HO_x in the upper troposphere than the reaction of the lowest-energy excited electronic state oxygen atom (O^1D_2) with water under upper tropospheric conditions.[1,5] Moreover, it is well known that heterogeneous processes taking place in or on hydrometeors play a crucial role in the reactions of many trace gases in the earth's atmosphere.[3] To quantify such heterogeneous processes, it is necessary to understand the rate of uptake of these trace gases by the condensed phase in addition to the partitioning of the reactants between the two phases. The partitioning of a compound between the gas phase and the liquid phase can be described at equilibrium and infinite dilution using Henry's law. The latter relates the gas partial pressure p_x (atm) to its liquid-phase concentration $c_{\mathrm{L},x}$ ($\mathrm{mol{\cdot}L^{-1}}$) at infinite dilution (eq 1).

$$c_{\mathrm{L},x} = H_x p_x \qquad (1)$$

In eq 1, H_x ($\mathrm{M{\cdot}atm^{-1}}$) is the Henry's law constant. Reactions of trace gas compounds in or on the hydrometeors depend on the partitioning of that compound in the liquid phase. Therefore, if chemical reactions are lacking or slow, then the concentration of a gaseous compound will be solely controlled by the equilibrium partitioning as described by Henry's law.[6] At present, the Henry's law constant for acetone has been extensively studied.[1,7−21] As a result, the measurement of the Henry's law constant for acetone was used to "test" the experimental approach used in this work. The reported Henry's law constant data for 2-butanone and 2,3-butanedione scatter considerably. The room-temperature Henry's law constants for 2-butanone are reported to vary by a factor of 15 from a value of $H_x = 6.9\ \mathrm{M{\cdot}atm^{-1}}$ to $105\ \mathrm{M{\cdot}atm^{-1}}$ (Table 2). Moreover, the values of $-\mathrm{d}(\ln H_x)/\mathrm{d}(1/T)$ for 2-butanone are reported to vary from (5200 to +5700) K (Table 3). To the best of our knowledge, only one temperature dependence study of the Henry's law constant for 2,3-butanedione has been reported to date.[13] Betterton[13] obtained a room-temperature $H_x = 74\ \mathrm{M{\cdot}atm^{-1}}$ and $-\mathrm{d}(\ln H_x)/\mathrm{d}(1/T) = 5700$ K. Two other room-temperature studies carried out by Gaffney and co-workers[22] and Snider and Dawson[23] report $H_x = 190\ \mathrm{M{\cdot}atm^{-1}}$ and $57\ \mathrm{M{\cdot}atm^{-1}}$, respectively.[10,11] To the best of our knowledge, no aqueous Henry's law constants have been reported for isobutyraldehyde.

As a result, new measurements of the Henry's law constants for 2-butanone, 2,3-butanedione, and isobutyraldehyde are warranted. In addition, all of the previous studies used other experimental techniques, namely, headspace or bubble-column techniques.[13] A comparison of data obtained from different experimental techniques is important because each technique is subject to different systematic errors.

Experimental Section

Materials. The reagents used in this work had the following stated minimum purities (in mass units): nitrogen (Air Liquide, >99.997%); acetone (Aldrich, HPLC grade, >99.9%); 2-butanone (Aldrich, ACS reagent, >99%); 2,3-butanedione (Aldrich, 97%); and isobutyraldehyde (Aldrich, 98%). Deionized water with a resistivity >18 MΩ cm was used. Deionized water was prepared by passing

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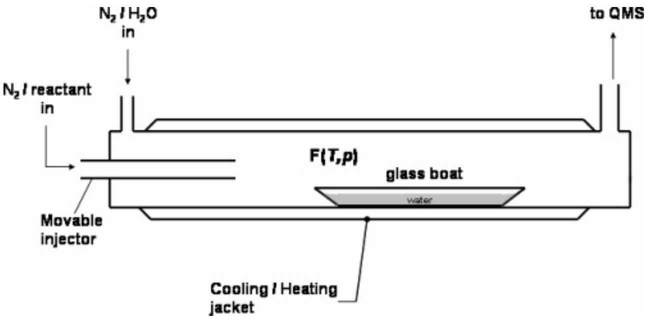


Figure 1. Schematic representation of the horizontal flow tube experimental approach used to measure Henry's law constants: QMS, quadrupole mass filter; $F(T, P)$.

tap water through a reverse osmosis demineralization filter (ATS Groupe Osmose) followed by a commercial deionizer (Millipore, Milli-Q^{50}). Henry's law constant experiments for acetone, 2-butanone, and 2,3-butanedione were performed in unbuffured water with a pH value of ~5.7. Henry's law constant measurements for isobutyraldehyde were performed at pH ~5.7 and 12.7.

Apparatus and Procedures. The flow tube approach used in this study is similar to the one used in previous studies of heterogeneous reactions. (See, for example, refs 24−26.] In addition, the horizontal flow reactor used in this work is similar to other proven experimental techniques, namely, the headspace, droplet train, and bubble-train flow reactors, where the gas-phase compound interacts with the liquid and the disappearance of that compound from the gas phase is monitored. However, the horizontal reactor has many practical advantages over other experimental techniques listed above, including (1) the ability to use small liquid volumes, (2) knowing the liquid volume exactly, (3) knowing the surface area, (4) easy data analysis, (5) the ability to carry out experiments under tropospheric and stratospheric conditions, and (6) no requirement for exact calibration.

The horizontal flow reactor experiments involve time-resolved detection of the organic reactant gas using molecular beam mass spectrometry after the reactant comes in contact with the liquid water surface. The schematic of the experimental approach is shown in Figure 1. Some experimental details that are relevant to this work are given below.

A jacketed, Pyrex reaction tube with a total internal volume of approximately 119 cm^3 was used in all experiments. The cell was maintained at a constant temperature (±0.5 K) (using a Huber CC130 thermostatically controlled bath) by circulating a 1:1 ethanol/methanol mixture through the outer jacket. A type J thermocouple (Omega Engineering, Inc.) with a stainless steel jacket was inserted into the reactor through a vacuum seal, allowing for the measurement of the temperature under the precise experimental conditions employed. The geometry of the flow tube reactor was such that it allowed for the nitrogen carrier and the reactant flows to enter at one end and the mass spectrometer to be located at the downstream exit at the opposite end.

All experiments were carried out at atmospheric pressure with the linear flow rate through the reactor in the range of (3 to 10) cm s^{-1}. Similar to the work of Hanson and Ravishankara,[25] the Pyrex tube was mounted horizontally, and the liquid water was contained within a glass "boat" that rested on the bottom, inside the Pyrex flow tube (Figure 1). The boat was made of glass and was 19 cm long. The open top of the boat was 1 cm wide and about 1 cm deep. As a result, the boat container could hold up to 10 cm^3 of water. Because the boat rested on the bottom of the horizontal flow tube, the resulting water surface was essentially planar.[25] Because the water surface was not renewed, water vapor was added to the N_2 carrier gas to avoid evaporation from the water surface and, therefore, maintain the liquid at its original volume and temperature. The reactant gas was introduced into the reactor via a 6.35-mm-o.d. and 500-mm-long movable glass injector equipped with a fritted end. Once the reactant gas entered the reaction cell, it was diluted by the nitrogen carrier gas, and the resulting gas mixture was allowed to come into contact with the liquid surface. The gas-phase reactant was monitored directly (i.e., the reactant gas was introduced directly into the differentially pumped chamber without any pretreatment or preconcentration) using a molecular beam mass spectrometer. The molecular mass of the reactant gas was monitored in multiple ion current detection (MID) mode (i.e., ion current vs time) using "soft" ionization energy (IE $\leq$ 20 eV) to obtain a maximum molecular ion current (peak) with the least fragmentation. Here, the monitored mass (mass-to-charge ratio, m/z) was known, and the system reported back only these points. That is, only the mass numbers of interest were determined and analyzed. At the same time, the ion current of an isotope of water ($m/z = 20$) was continuously monitored to test and make sure that the system remained stable when the injector was inserted and withdrawn within the reactor. Numerous tests were performed to ensure that it was actually the reactant gas that was detected and not some impurity present in the system or the reaction cell. The observed intensity of the product ion current signal was proportional to the concentration of the neutral reactant gas. The ion signal was observed to increase linearly with increasing reactant gas concentration over the concentration range used in this work. A possible source of error may result from the mass spectrometer background (background gases). It consists of gases that are present in the vacuum system that do not come from the sample to be measured. As a result, the background signal was recorded by the zero gas measurement and subtracted from the subsequent MID measurements. In this way, the resulting ion current was composed of only the real "parts" of the analyzed gas.

A typical experiment was initiated by allowing the N_2 + H_2O + organic reactant gas (where organic reactant gas = acetone, 2-butanone, 2,3-butanedione, or isobutyraldehyde) mixture to flow through the reactor with the injector positioned all the way in at the entrance of the mass spectrometer inlet. At this point, signal S_0 was obtained (i.e., the liquid water surface was not exposed to the organic reactant gas). Then the injector was quickly moved back to expose a known volume of water to the reactant, and the resulting gas-phase concentration of the organic reactant gas was monitored as a function of time. The time at which the injector was moved back to expose the liquid water surface is defined as t_1. A decrease in the signal (an observed "drop" in the ion current) due to uptake by the liquid was observed. The signal recovered slowly with time to S_0 as the liquid became saturated with the absorbent. After the liquid was observed to be saturated (ion current at the S_0 level), the inlet was moved all the way in so that the liquid water surface was no longer exposed to the absorbent gas. Here, the signal was observed to increase to greater than S_0 because the absorbed gas evaporated from the liquid into the carrier gas and was added to the gas flow from the inlet. Afterward, the signal decayed back to S_0 as the dissolved gas was fully evaporated from the liquid volume. The above procedure was repeated in a dry environment where no water was present in the "boat". Moving the injector back and forth in a dry reactor did not produce any change in the observed ion current signal. The Henry's law constants were determined by measuring the quantity of the organic reactant gas absorbed by a known volume of water.[24,27] The main advantages of measuring the temporal profile of the concentration of the organic reactant gas that was suddenly exposed to a known volume of water are that determinations of absolute concentrations and a knowledge of the diffusion constant D are not necessary.[24,27] Moreover, it was assumed that gas-phase diffusion is fast and that no considerable radial concentration gradient exists.[28−30]

The observed time scale needed to saturate the liquid phase with the gas-phase compound ranged from a few minutes to a few hours and was mostly dependent on the flow rate at which the gases were injected into the flow reactor (i.e., increasing the flow rate decreased the saturation time). The fastest observed saturation times were on the order of a few minutes, which is considerably shorter than just mixing through a diffusion process. In most experiments, the thickness of the aqueous phase resting in the flow tube was just a few millimeters, which can easily be affected by any unwanted vibrations (for example, those due to the MS pumping system or the cryostat) or surface turbulence due to the reactor geometry and potentially high flow rates. However, this does not affect our experiments because the time needed to achieve saturation was systematically monitored.

Our measurement resulted in a dimensionless Henry's law constant (H_xRT), which is the ratio of the liquid-phase number density to the number density of molecules in the gas phase at equilibrium.[24,25] At each temperature, two to three experiments were carried out. The Henry's law constant was calculated using eq 2 adopted from the work of Hanson and Lovejoy:[24]

$$H_x = \frac{I(t)F}{S_0 V_{H_2O} RT} \tag{2}$$

In eq 2 above,

$$I(t) = |S_0 t - \int_{t_1}^{t_2} S(t)\,dt|$$

and is the area (integral) of the signal over time below or above the baseline signal S_0,[24] F (cm^3 min^{-1}) is the total mass flow rate, and V_{H_2O} (mL) is the liquid volume in the reactor.[24] In this work, the area of the signal over time below S_0 (uptake traces) was used to calculate the Henry's law constant. However, no difference in the Henry's law constant value was observed if either trace (uptake or evaporation trace) was used. The Henry's law constant can be described as a function of temperature using eq 3, given by

$$H_x = H_x^0 \exp\left(\frac{-\Delta_{\text{solution}}H}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right)\right) \tag{3}$$

where H_x is the Henry's law constant, H_x^0 is the Henry's law constant under standard conditions (T^0 = 298.15 K), and $\Delta_{\text{solution}}H$ is the enthalpy of solution. Equation 3 can be rearranged to give the temperature dependence of the Henry's law constant (eq 4):

$$\frac{-\text{d} \ln H_x}{\text{d}(1/T)} = \frac{\Delta_{\text{solution}}H}{R} \tag{4}$$

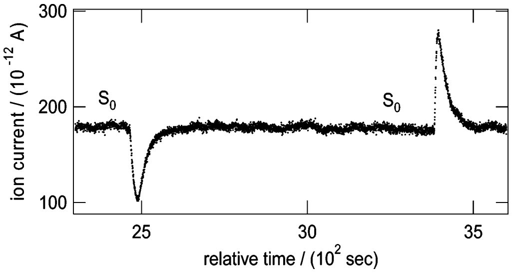


Figure 2. Typical ion current signal for absorption and evaporation of acetone; experimental conditions: T = 278 K, p = 1013 hPa Torr, V_{liquid} = 5 mL.

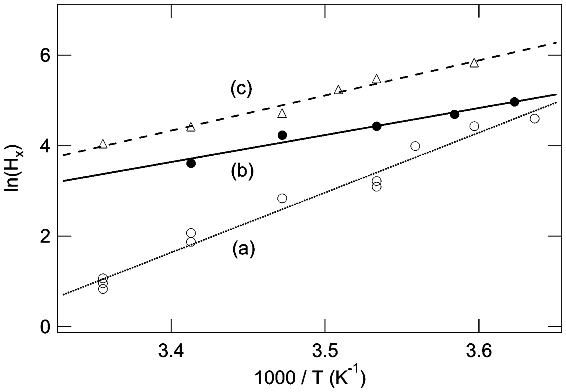


Figure 3. Plots of ln(H_x) versus T^{-1} for (a) 2-butanone, (b) acetone, and (c) 2,3-butanedione obtained for the following temperature ranges: (a) (275 to 298) K, (b) (276 to 293) K, and (c) (278 to 298) K. Solid lines are obtained from a linear least-squares analysis. The values of r^2 for the regression lines are (a) 0.99, (b) 0.98, and (c) 0.99.

Concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates, vapor pressure, and total pressure. The mass flow rates were determined using Brooks electronic mass flow meters, which had a range of 100 to 1000 standard cm^3·min^{-1} (sccm). The reaction cell pressure was measured using an active Pirani gauge (Edwards High Vacuum Int.). The N_2 buffer gas was allowed to flow directly from its high-pressure storage tank. The reactant flow was obtained by allowing a known flow rate of nitrogen gas to pass through a thermostatically controlled bubbler that contained the organic reactant liquid. The organic reactant concentration was determined using certain known parameters, namely, the nitrogen mass flow rate, the organic reactant vapor pressure at a temperature T, and the total pressure. Likewise, water vapor was added by allowing the nitrogen gas to pass through a flask containing deionized H_2O. The water vapor content was determined using Antoine equation parameters for the temperature range of T = (273 to 303) K.[31] The organic reactant concentration was kept below 50 ppm.

Results and Discussion

Acetone. A typical signal for the variation of the acetone gas-phase concentration as a function of time during dissolution into a known volume of water followed by evaporation is shown in Figure 2. The plot of ln(H_x) versus T^{-1} for acetone is shown in Figure 3. The results of all experiments are summarized in Table 1. The observed temperature dependence of the Henry's law constant for acetone is found to agree well with the literature.

A comparison of the reported Henry's law constants for acetone is summarized in Table 2. Also, we find that the

Table 1. Summary of the Measured Henry's Law Constant Data Obtained in This Work

p/hPa	T/K	V_{liquid}/mL	flow/cm^3·s^{-1}	H_x/M·atm^{-1}
		Acetone		
1017	276	5	550	144(±30)
1017	279	5	550	109(±22)
1017	283	5	552	84(±18)
1017	288	5	554	69(±14)
1017	293	5	558	37(±8)
		2-Butanone		
1022	275	5	778	81(±10)
1022	278	5	666	73(±9)
1022	281	5	779	47(±6)
1022	283	5	555	25(±3)
1022	283	5	665	22(±3)
1022	288	5	669	17(±2)
1022	293	5	671	7.9(±0.9)
1022	293	5	671	6.5(±0.8)
1022	298	5	452	2.3(±0.3)
1022	298	5	452	2.6(±0.3)
1022	298	5	452	2.9(±0.3)
		2,3-Butanedione		
1032	278	2	783	267(±36)
1017	283	2	775	202(±30)
1017	285	2	777	182(±30)
1017	288	2	787	112(±17)
1017	293	2	783	83(±12)
1027	298	2	789	57(±8)
		Isobutyraldehyde		
1013	275	5	550	2.11(±0.5)
1008	275	5	332	2.06(±0.06)[a]
1008	275	5	332	2.10(±0.06)[a]
1008	276	5	331	2.00(±0.28)
1013	279	5	332	1.60(±0.24)
992	281	5	333	1.32(±0.20)
992	281	5	224	1.34(±0.20)
1026	283	5	223	1.32(±0.20)
1008	283	5	334	1.33(±0.20)[a]
1008	283	5	334	1.34(±0.20)[a]
997	285	5	280	1.03(±0.15)
997	285	5	280	1.06(±0.16)
992	288	5	281	1.08(±0.16)
992	288	5	226	1.05(±0.16)
997	290	5	281	0.81(±0.17)
997	290	5	281	0.93(±0.17)
1026	293	5	226	0.77(±0.12)
772	293	5	226	0.74(±0.11)

[a] All experiments were carried out at pH ~5.7, except where where the pH is ~12.7. Stated uncertainties are ±2σ.

observed room-temperature Henry's law constant agrees well with the reported values (Table 2). Therefore, on the basis of the results obtained in this work for the Henry's law constant for acetone we can report that the experimental approach used in this study gives results that are in good agreement with the previously reported data for acetone using other well-established and proven techniques.

Also in our experimental approach, the gas-phase compounds are directly exposed to the aqueous-phase surfaces leading to a potential surface accumulation of the organics. This could be an important effect here because the surface-to-volume ratio was typically on the order of 4 cm^{-1}. However, as shown in Table 2 for acetone, our data compares favorably to almost all reported values. We therefore believe that this was not a serious issue in the course of these experiments.

2-Butanone. A typical signal for the variation of the 2-butanone gas-phase concentration as a function of time during uptake by the liquid is similar to that of acetone shown in Figure 2. The plot of ln(H_x) versus T^{-1} for 2-butanone is shown in Figure 3. The results of all experiments are summarized in Table 1. The Henry's law constants for 2-butanone obtained in this study are compared with other published data in Table 3. We find that the room-temperature Henry's law constant falls on the lower limit of the reported values (Table 3). In fact, the value of H_x for 2-butanone obtained in this work is the lowest of any previously measured values. In addition, a much stronger temperature dependence is observed for the Henry's law constant for 2-butanone compared with the literature data. At this point, we are not able to explain the observed strong temperature dependence of H_x for 2-butanone. However, all previous measurements of H_x were performed using headspace or bubble-column techniques. An analysis of the oxygenated compounds (i.e., aldehydes and ketones) using these techniques is difficult because they have relatively low Henry's law constants.[32] Moreover, other experimental techniques listed above require precise calibrations. Such precise calibrations are not required using the experimental approach used in this study.

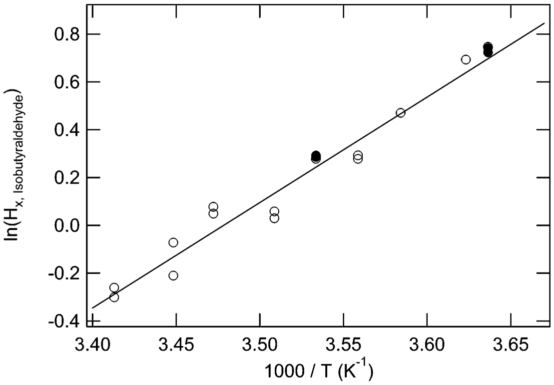


Figure 4. Plots of ln(H_x) versus T^{-1} for isobutyraldehyde data obtained in the temperature range of (275 to 293) K. The solid line is obtained from a linear least-squares analysis. Experimental conditions: ○, pH ~5.7; ●, pH ~12.7. The value of r^2 for the regression line is 0.98.

2,3-Butanedione. The signal for the variation of the 2,3-butanedione gas-phase concentration as a function of time during uptake by the liquid is similar to the acetone signal shown in Figure 2. The plot of ln(H_x) versus T^{-1} for 2,3-butanedione is shown in Figure 3. The results of all experiments are summarized in Table 1. The Henry's law constants for 2,3-butanedione obtained in this study are compared with other published data in Table 4. The room-temperature Henry's law constant is reported to be 57 M·atm^{-1}, and $\Delta H/R$ is reported to be 7800 K. The recommended temperature dependence of H_x for 2,3-butanedione is based solely on one experimental work carried out by Betterton.[13] This investigator reports H_x = 74 M·atm^{-1} at T = 298 K and $-\mathrm{d}\ln H_x/\mathrm{d}(1/T)$ = 5700 K.[13] Two other room-temperature studies report H_x for 2,3-butanedione to be 190 M·atm^{-} [10] and 57 M·atm^{-1}.[11] The room-temperature Henry's law constant and the temperature dependence of H_x reported in this work agree well with the currently recommended values by Snider and Dawson[11] and Betterton.[13]

Isobutyraldehyde. The signal for the variation of the isobutyraldehyde gas-phase concentration as a function of time during uptake by the liquid is similar to that of acetone shown in Figure 1. The plot of ln(H_x) versus T^{-1} (K^{-1}) for isobutyraldehyde is shown in Figure 4. The results of all experiments are summarized in Table 1. The Henry's law constants for isobutyraldehyde obtained in this study are shown in Table 5. To our knowledge, there are no other

Table 2. Comparison of the Reported Henry's Law Constants for Acetone at T = 298 K

reference	H_x/M·atm^{-1}	[−d ln H_x/d(1/T)]/K	type
Butler and Ramchandani[7]	30		recalculation
Burnett[8]	28		measured
Hine and Weimar[9]	3.1		recalculation
Buttery[37]	25		measured
Gaffney et al.[22]	30		measured
Snider and Dawson[11]	26	4800	measured
Zhou and Mopper[12]	35	3800	measured
Betterton[13]	32	5800	measured
Benkelberg et al.[14]	27	5300	measured
Vitenberg et al.[15]	25		measured
Hoff et al.[17]	27		measured
Yaws and Yang[18]	23		measured
Schaffer and Daubert[21]	22	5000	literature review
Janini and Quaddora[19]	3.0	3300	literature review
Staudinger and Roberts[20]	30	4600	literature review
this work	(26 ± 6)[a]	(6400 ± 1600)	

[a] T = 293 K. The Henry's law constant at T = 293 K has been recalculated for 298 K using the $\Delta_{\text{solution}}/R$ recommended in this work. The Table and references therein have been adopted from the original compilation of Henry's law constants by Sander[36] and appear as they were.

Table 3. Comparison of the Reported Henry's Law Constants at T = 298 K for 2-Butanone[a]

reference	H_x/M·atm^{-1}	[−d lnH_x/d(1/T)]/K	type
Hine and Weimar[9]	7.1		recalculation
Snider and Dawson[11]	18	5700	measured
Buttery et al.[37]	21		measured
Ashworth et al.[38]	7.7		literature review
Zhou and Mopper[12]	20	5000	measured
Howe et al.[39]	4.1 to 7.7		literature review
Vitenberg et al.[15]	18		measured
Rohrschneider[40]	19		measured
Friant and Suffet[41]	10		measured
Staudinger and Roberts[20]	20	5000	literature review
Ashworth et al.[38]	6.9	−5200	literature review
Janini and Quaddora[19]	7.2	5800	literature review
Betterton[13]	105		
Snider and Dawson[23]	58		
this work	(2.7 ± 0.3)	(12000 ± 5000)	measured

[a] The Table and references therein have been adopted from the original compilation of Henry's law constants by Sander[36] and appear as they were.

Table 4. Comparison of the Reported Henry's Law Constants at T = 298 K for 2,3-Butanedione[a]

reference	H_x/M·atm^{-1}	[−d lnH_x/d(1/T)]/K	type
Gaffney et al.[22]	190		measured
Snider and Dawson[11]	57		measured
Betterton[13]	74	5700	measured
this work	(57 ± 8)	(6700 ± 2400)	measured

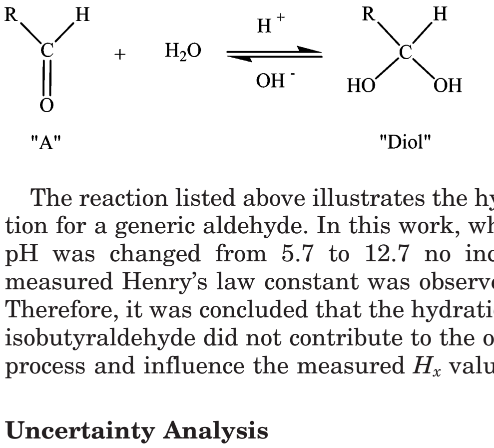
[a] Uncertainties in the H_x and −d ln H_x/d(1/T) values listed in this work are ±2σ. The Table and references therein have been adopted from the original compilation of Henry's law constants by Sander[36] and appear as they were.

Table 5. Reported Henry's Law Constant for Isobutyraldehyde[a]

reference	H_x/M·atm^{-1b}	[−d ln H_x/d(1/T)]/K	type
this work	(0.60 ± 0.10)	(4500 ± 2900)	measured

[a] Uncertainties in the H_x and −d ln H_x/d(1/T) values listed are below ±2σ. [b] This measurement was not at exactly 298 K. The value has been recalculated for 298 K by using the $\Delta_{\text{solution}}H/R$ value recommended in this work.

data available for aqueous Henry's law constants for isobutyraldehyde with which to compare our results. Because aldehydes can hydrate[33,34] to form "diols," experiments were carried out at pH ~5.7 and 12.7. This was done to demonstrate that the hydration reaction (eq 5) did not contribute to the overall uptake of isobutyraldehyde on water and influence the measured Henry's law constant.



$$K_{Hyd} = \frac{a_{Diol}}{a_A a_{H_2O}} \qquad (5)$$

The reaction listed above illustrates the hydration reaction for a generic aldehyde. In this work, when the water pH was changed from 5.7 to 12.7 no increase in the measured Henry's law constant was observed (Figure 4). Therefore, it was concluded that the hydration reaction of isobutyraldehyde did not contribute to the overall uptake process and influence the measured H_x value.

Uncertainty Analysis

At each temperature, two to three experiments were carried out. The mean H_x values for acetone, 2-butanone, 2,3-butanedione, and isobutyraldehyde are listed in Table 1. The uncertainties in the Henry's law constants measured in this study were evaluated using the propagation of error calculations discussed by Cvetanovic et al.[35] The overall error in H_x depended on the errors in all of the measurements involved (i.e., S_0, $I(t)$, F, V_{H_2O}, T, etc. and the time interval Δt (eq 7)):

$$H_x = f(S_0, I(t), F, V_{H_2O}, T, ..., \Delta t) \qquad (7)$$

The major assumption was that the time measurements were free from error and that the errors in the measurements involved were independent of each other. The cumulative value of the 2 standard deviations $2\sigma_{H_x}$ of H_x (95% confidence limit) was calculated using eq 8 adopted from the work of Cvetanovic et al.[35]

$$\frac{\sigma_{H_x}}{H_x} = 2\left\{\left(\frac{\sigma_{S_0}}{S_0}\right)^2 + \left(\frac{\sigma_{I(t)}}{I(t)}\right)^2 + \left(\frac{\sigma_F}{F}\right)^2 + \left(\frac{\sigma_{H_2O}}{V_{H_2O}}\right)^2 + \left(\frac{\sigma_T}{T}\right)^2 + ...\right\}^{1/2} \qquad (8)$$

In eq 8, σ_{S_0}, $\sigma I(t)$, σV_{H_2O}, σF, and σT are the computed or estimated standard deviations in the measured initial signal, integrated signal, liquid water volume, flows, and temperature, respectively.

Temperature Trends

In Tables 2 to 5, we also report the slope of the plots of $\ln(H_x)$ versus T^{-1} (K^{-1}), which using the van't Hoff equation (eq 4) corresponds to the enthalpy of solvation divided by the ideal gas constant R (i.e., the slopes equal $-\Delta H_{solution}/R$). For all species investigated here and within the considered temperature range, all of these plots were linear, highlighting the fact that $\Delta H_{solution}$ is temperature-independent between 275 and 300 K.

The derived enthalpies of solvation are the following (in units of kJ mol^{-1}): $-(53 \pm 13)$ for acetone, $-(99 \pm 41)$ for 2-butanone, $-(56 \pm 20)$ for 2,3-butadione, and $-(37 \pm 24)$ for isobutylraldehyde. The quoted errors for $\Delta H_{solution}$ are given at the 2σ level as derived from the error analysis given above.

In Tables 2 to 5, we also compare these values to previously reported data (when available). With the exception of 2-butanone, all data compares favorably within the reported error range.

Also, these values are relatively close to the average value of $-\Delta H_{solution}/R$ derived Staudinger and Roberts in their compilation[20] (i.e., almost 5000 K as an average while all data were spanning over the range from 290 to 10 500 K). It is worth noting that all data report here are also within this range.

Conclusions

In this work, the Henry's law coefficients for acetone, 2-butanone, 2,3-butanedione, and isobutyraldehyde were measured using a horizontal flow reactor. All experiments were performed at atmospheric pressure and temperature over the range of 275 to 298 K. The Henry's law constants at $T = 298$ K are the following (in units of M·atm^{-1}): acetone, (26 ± 6); 2-butanone, (2.7 ± 0.3); 2,3-butanedione, (57 ± 8); and isobutyraldehyde, (0.60 ± 0.10). The uncertainties listed above are $\pm 2\sigma$ and have been calculated using the propagation of errors analysis discussed above. In experiments where the temperature was not exactly 298 K, H_x has been recalculated for 298 K by using the $\Delta_{sol}H/R$ value recommended in this work. We find that the Henry's law constants for acetone agree well with the literature using other well-established techniques. However, the room-temperature value of H_x for 2-butanone is the lowest measured so far. Moreover, the observed temperature dependence of the Henry's law constant for 2-butanone is much stronger than previously reported. The room-temperature Henry's law constant and the temperature dependence of H_x for 2,3-butanedione reported in this work agree well with the work by Snider and Dawson[11] and Betterton[13] but are a factor of 3 to 4 lower than the values reported by Gaffney and co-workers.[22] The observed temperature dependence of the Henry's law constant for 2,3-butanedione agrees well with the only other temperature-dependence study carried out by Betterton.[13] There are no Henry's law constants for isobutyraldehyde reported with which to compare our results.

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